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Spatiotemporal Variation Characteristics and Source Identification of Nitrogen in the Baiyangdian Lake Water, China

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Abstract: To study the characteristics and sources of nitrogen in the Baiyangdian Lake, this research conducted water quality monitoring during three hydrological periods (normal period, flood period, and dry period), and 165 pieces of routine water quality monitoring data were collected from the three national control sections for Baiyangdian Lake and its inflow rivers. By integrating water chemical analysis with multivariate statistical techniques, the study comprehensively investigated the spatiotemporal variation patterns of nitrogen in Baiyangdian Lake and identified the sources of nitrogen pollution. The results showed that the concentration of total nitrogen (TN) was highest during the dry period, reaching an average of 0.924 mg/L, and 31.3% of the sites exceeded the national Grade III surface water quality standard, reflecting a potential risk of nitrogen pollution. Based on the ion ratio method and principal component analysis (PCA), the main sources of nitrogen pollution in Baiyangdian Lake were identified as manure and domestic sewage, with agricultural fertilizers also having a certain impact on water nitrogen pollution. In addition, the study also compared the nitrogen concentration in Baiyangdian Lake with several important lakes in China. The results showed that the concentrations of TN and ammonium nitrogen (NH_4^+-N) in Baiyangdian Lake are lower than those in lakes in areas with similar human activity intensity, indicating that the water quality of Baiyangdian is relatively good. This study can provide a scientific basis for water quality management and pollution prevention for Baiyangdian Lake.

Keywords: lakes; nitrogen; water quality; source identification; principal component analysis

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1. Introduction

Lakes are vital water resources that play an irreplaceable role in regional environmental changes, biogeochemical cycling, ecological function maintenance, safeguarding water supply security, preserving biodiversity, and fostering socio-economic development within their catchment areas [1–3]. However, the increasing intensity of human activities has led to a significant influx of nutrients, such as nitrogen, into lake waters, causing eutrophication and water quality deterioration and severely impacting the ecological functions and value of these lakes [4]. Therefore, studying the spatiotemporal variations of nitrogen in lakes and elucidating its pollution sources is of significant importance for guiding the management of water environmental pollution in lakes [5].

The factors influencing the spatiotemporal variations of nitrogen in lake waters primarily consist of natural and anthropogenic factors [6]. Natural factors, such as seasonal variations in rainfall, can significantly influence the spatiotemporal dynamics of nitrogen within lake waters, specifically manifesting in two aspects: First, rainfall dilutes the concentration of nitrogenous nutrients in lake water, showing a temporal pattern where nitrogen concentrations are lower during the flood season compared to other seasons [7]. Second, the concentration of nitrogen in a lake is affected by the scouring action of rainfall; runoff from rainfall carries nitrogen retained on agricultural and urban surfaces into the lake, leading to higher nitrogen concentrations in the lake water during the flood season than during the dry season [8]. Additionally, the migration and transformation processes of nitrogen in the water body (such as nitrification and denitrification) significantly affect the changes in nitrogen load [9].

Anthropogenic factors affecting the spatiotemporal variations of nitrogen in lakes include various industrial and agricultural activities, domestic sewage, urban development, and land use practices. Yu et al. (2015) found that the spatial differences in land use practices in Xiaoxingkai Lake were the main reasons for the significant differences in nitrate nitrogen (NO_3^--N) and ammonium nitrogen (NH_4^+-N) concentrations between the eastern and western parts of the lake, leading to water quality disparities [10]. Mbaye et al. (2016) conducted a study on the spatiotemporal variations of nitrogen in Lake Senegal and found that the concentrations of NO_3^--N and total nitrogen (TN) were significantly higher in the densely populated areas and areas with intensive agricultural development downstream than in the upstream areas of the lake [11]. Zhang et al. (2017) discovered that there was a strong spatial variability in NO_3^--N and NH_4^+-N in the Fuyang River, with higher concentrations near urban areas and lower concentrations in areas farther from the city, where the water quality was in a state of severe eutrophication throughout the year [12]. It is evident that the characteristics of spatiotemporal variations of nitrogen in an aquatic environment are influenced by a combination of natural conditions and human activities. Different lakes exhibit similarities and differences in the spatiotemporal characteristics of nitrogen due to their distinct regional rainfall patterns and sources of nitrogen. Therefore, to accurately identify the spatiotemporal patterns of nitrogen in lakes, comprehensive surveys and systematic research are necessary.

Baiyangdian is the largest lake in the North China Plain and one of the few remaining lake-type wetland ecosystems in the region [13]. It is strategically located at the core of the Xiong'an New Area and plays a significant role in flood control, navigation, fisheries, and climate regulation, providing crucial ecological support for the development of the Xiong'an New Area [14]. In recent years, due to the development of industry and agriculture and the increasing demand for water resources in the basin, Baiyangdian Lake has been facing water pollution issues, which have become a critical problem that urgently needs to be addressed for the development of the Xiong'an New Area [15]. Scholars have conducted extensive research on water environmental quality issues [16], the decline in biodiversity of biological communities [17], and heavy metal pollution issues [18] in the Baiyangdian watershed. However, research on the spatiotemporal variation patterns of nitrogen and the identification of pollution sources in Baiyangdian Lake is still relatively weak, which severely restricts the progress of water environment restoration efforts in Baiyangdian Lake.

This study selects Baiyangdian Lake as the research subject. By integrating hydrogeological and geochemical methods with multivariate statistical techniques, this research aims to identify the spatiotemporal variation characteristics of nitrogen in Baiyangdian Lake, assess the water quality, and reveal the main sources of nitrogen pollution. The goal is to provide a scientific basis for the comprehensive management of the Baiyangdian water environment and for the protection of water environments in lakes.

2. Materials and Methods

2.1. Introduction to the Study Area

Baiyangdian Lake is located between 115°38′ E to 116°07′ E longitude and 38°43′ N to 39°02′ N latitude, primarily situated within the territory of Anxin County, Baoding City, Hebei Province, China (see Figure 1). This area belongs to the Daqing River sub-basin system of the Hai River basin, with a basin area of approximately 366 square kilometers. Within its vast wetland ecosystem, there are 143 lakes of varying sizes, with an average water depth of about 2.3 m. The climate of the region is characterized as a temperate semi-humid continental monsoon climate, with distinct seasons. Spring is usually dry with strong winds and scarce rainfall; summer is relatively hot with abundant rainfall, mainly concentrated from July to September. According to long-term meteorological records, the average temperature of the area is about 12.2 °C, and the average annual precipitation is about 529.7 mm. The soil types in the basin are diverse, including tidal soil, swamp soil, brown soil, and paddy soil, among others. Land use types encompass a variety of categories such as forest land, farmland, construction land, grassland, and water bodies. The water flow direction in the Baiyangdian basin generally exhibits a northeastward flow from west to east. The water source is mainly replenished by nine major rivers entering the lake: the Zhulong River, Xiaoyi River, Tang River, Qingshui River, Bao River, Fu River, Ping River, Cao River, and BaigouYin River. In addition, ecological water replenishment measures, such as the Yellow River Diversion Project and the South-to-North Water Diversion Project, also provide important supplementary water resources for the area.

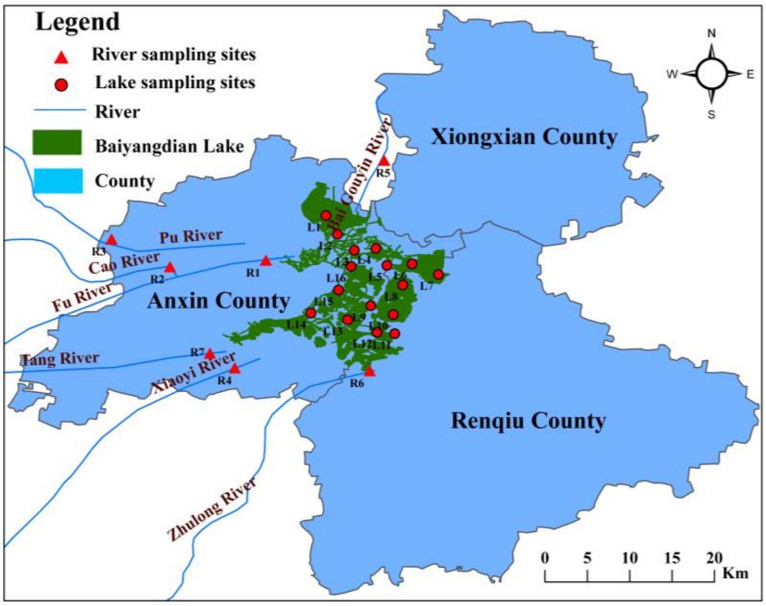


Figure 1. Distribution map of sampling points in Baiyangdian Lake.

2.2. Sample Collection and Analysis

In this study, a total of 16 sampling points were established in Baiyangdian Lake and 7 in the rivers. Sampling was conducted three times: in May 2022 (normal season, spanning from March to May and October to November), in July 2022 (flood season, from June to September), and in December 2022 (dry season, from December to February of the following year, when the lake was under an ice cover). Samples were collected in 2.5 L polyethylene bottles, which were rinsed three times with lake water before sampling. Surface water samplers were used to collect samples at a depth of 0.5 m from the river surface. After collection, the samples were sealed, placed in a refrigerated box, and transported back to the laboratory. They were then filtered through a 0.45 µm glass fiber filter membrane and stored in a 4 °C refrigerator. All samples were tested within 48 h. In addition, 165 pieces of routine water quality monitoring data were collected from the three national control sections (corresponding to sites L1, L5, and L12 in this study) of Baiyangdian Lake from 20 May 2022 to 22 November 2022. These three routine monitoring sites are located in the north, center, and south of the study area, respectively, and can represent the overall water quality situation of Baiyangdian Lake.

The testing indicators mainly included total nitrogen (TN), ammonium nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^--N), calcium (Ca^{2+}), sodium (Na^+), sulfate (SO_4^{2-}), and chloride (Cl^-). For water chemical analysis: anions (Cl^- and SO_4^{2-}) were determined using an ion chromatograph (Perkin-Elmer Lambda 35, San Diego, CA, USA), and bicarbonate (HCO_3^-) was measured by standard dilute hydrochloric acid titration; cations (Ca^{2+} and

Na^+) were analyzed using an inductively coupled plasma-mass spectrometry (Agilent 7500ce, ICP-MS, Tokyo, Japan). NH_4^+-N was measured using the Kjeldahl method with Nessler's reagent; TN was determined using the alkaline potassium persulfate digestion ultraviolet spectrophotometry method, and NO_3^--N was measured using the phenol disulfonic acid spectrophotometric method with an error less than 0.05 mg/L. Sample quality control (QA-QC) involved conducting tests on blank, duplicate, and standard samples. Each sample was tested three times to ensure accuracy. Furthermore, the data on TN concentration from the three national control sites were collected from the Ministry of Ecology and Environment's National Control Section Monitoring Website in China.

2.3. Data Analysis

2.3.1. Principal Component Analysis

Principal component analysis (PCA) is a mathematical transformation method that converts a given set of correlated variables into another set of uncorrelated variables through linear transformation. These new variables are arranged in descending order of variance. The total variance of the variables remains unchanged during the transformation, with the first variable having the maximum variance, referred to as the first principal component. The second variable has the next highest variance and is uncorrelated with the first, known as the second principal component, and so on, with the last principal component having the smallest variance and being uncorrelated with all previous components.

PCA is a well-established multivariate statistical analysis method that incorporates multidimensional factors into a unified system for quantitative research. In this study, PCA is employed to identify the main pollution sources of nitrogen in the Baiyangdian Lake. The analysis was based on seven selected water quality parameters, namely, TN, NO_3^--N, NH_4^+-N, Na^+, Ca^{2+}, SO_4^{2-}, and Cl^-. Prior to the application of the data to the PCA model, the study data underwent the Kaiser–Meyer–Olkin (KMO) test and Bartlett's test of sphericity. The results indicated that for the normal, flood, and dry seasons, the KMO values were 0.576, 0.656, and 0.565, respectively, and the Bartlett's test values were 38.4 ($p < 0.01$), 123.5 ($p < 0.001$), and 63.8 ($p < 0.001$), respectively. These findings suggest that the water chemistry data of Baiyangdian Lake for the three hydrological periods meet the requirements for PCA. Based on an eigenvalue >1, two principal components were identified for each of the three hydrological periods, which accounted for 64.1%, 80.6%, and 67.5% of the total variance in the data, respectively.

2.3.2. Cluster Analysis

Cluster analysis is one of the most widely used exploratory methods and can be divided into two categories: variable clustering (R-type clustering) and sample clustering (Q-type clustering). The essence of cluster analysis is to group objects that are most similar based on the degree of closeness between variables or samples, using a stepwise aggregation method until they form a single cluster. In water quality assessment, clustering is often performed based on sampling points and times to analyze the spatiotemporal variation characteristics of water quality or based on evaluation indicators to analyze the similarities between indicators. In this study, the inter-group Euclidean distance method is used to analyze the sampling sites in Baiyangdian Lake through cluster analysis. Additionally, we calculated the silhouette coefficients for the clustering analysis results of three hydrological periods. The results showed that 83%, 92%, and 92% of the silhouette values in the normal flow period, flood season, and dry season clustering analysis results were greater than 0.5, indicating that the clustering results are relatively accurate.

The raw water chemistry data for surface water were organized and statistically analyzed using Excel 2021. Ion concentration ratio plots (Cl vs. NO_3^-) were created using Origin 2021 (2019b), and sampling point distribution maps were generated using ArcGIS 10.8. Cluster analysis and principal component analysis plots were created using R 4.4.1.

3. Results and Analysis

3.1. Temporal Variation Characteristics of Nitrogen Concentration in Baiyangdian Lake

3.1.1. Temporal Variation of Nitrogen Concentration in Baiyangdian Lake

Table 1 summarizes the concentration changes of TN, NO_3^--N, and NH_4^+-N in Baiyangdian Lake during different hydrological periods. The temporal variation of TN shows that the average concentration during the dry season (0.924 mg/L) is higher than that during the flood season (0.786 mg/L) and the normal water period (0.759 mg/L). As shown in Figure 2, the temporal variation of TN concentrations at the three routine monitoring sites in the Baiyangdian Lake water body exhibits higher levels during the dry and normal periods compared to the flood season. This is mainly related to the insufficient water replenishment during the dry season, which cannot dilute the pollutants within the lake. Additionally, the concentrations of sites 2, 3, and 5 exceed the Class III standard (1.0 mg/L) of the surface water environmental quality standard of China during the normal, flood, and dry seasons, respectively, indicating that the Baiyangdian Lake still faces a risk of nitrogen pollution. The concentration of NO_3^--N ranges from 0.020 to 1.35 mg/L, 0.130 to 1.07 mg/L, and 0.101 to 2.01 mg/L during the normal, flood, and dry seasons, respectively. Its temporal variation shows that the concentration is highest during the normal water period (0.559 mg/L), followed by the dry season (0.528 mg/L), and lowest during the flood season (0.380 mg/L), which is mainly related to the dilution effect of rainfall during the flood season. Furthermore, the concentration of NH_4^+-N is relatively low, with 70% of the sampling sites having NH_4^+-N concentrations below the detection limit of 0.025 mg/L. Its temporal variation also shows that the concentration is lowest during the flood season (0.025 mg/L) and the normal water period (0.025 mg/L), and highest during the dry season (0.131 mg/L). Overall, the coefficient of variation for the three indicators is higher during the dry season than during the flood season, indicating that the larger replenishment flow of rivers during the flood season not only promotes adequate mixing of the water in the lake area but also effectively reduces the variability of the indicators in the water body.

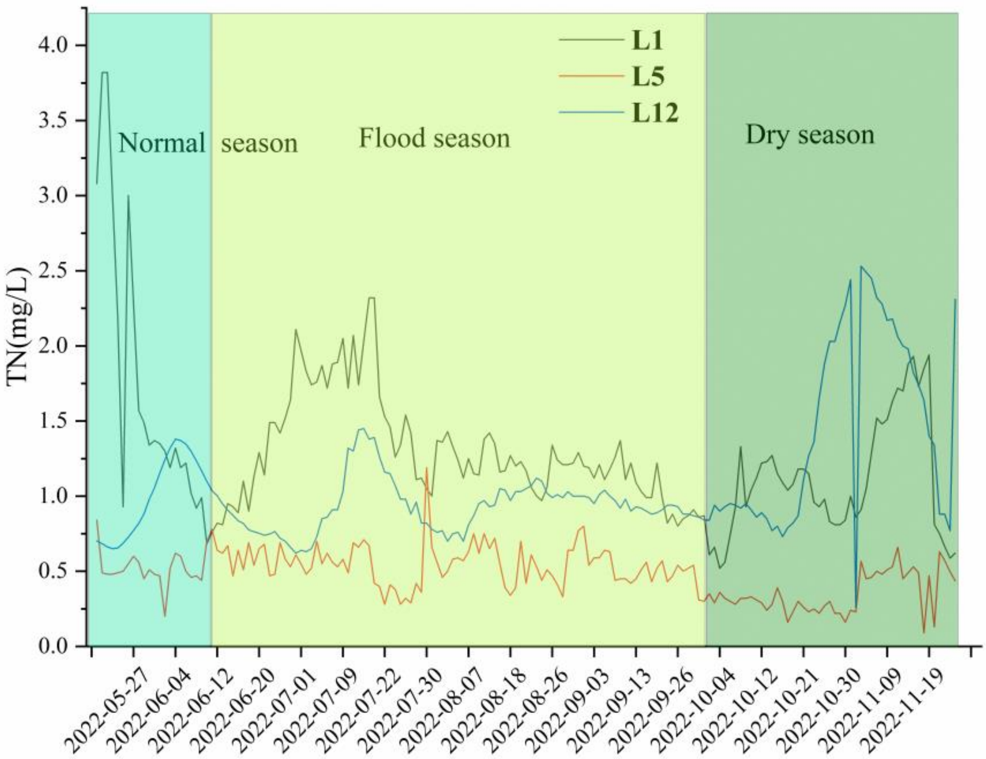


Figure 2. Temporal variation of TN in the Baiyangdian Lake.

Table 1. Statistics of different nitrogen concentrations in Baiyangdian Lake.

Parameters	Season	Mean (mg/L)	Min (mg/L)	Max (mg/L)	Standard Deviation	Coefficient of Variation (%)
TN	Normal Season	0.759	0.450	1.98	0.401	52.7
	Flood season	0.786	0.502	1.54	0.313	39.8
	Dry season	0.924	0.532	2.51	0.536	58.0
NO_3^--N	Normal Season	0.559	0.020	1.35	0.278	49.7
	Flood season	0.380	0.130	1.07	0.256	67.4
	Dry season	0.528	0.101	2.01	0.522	98.9
NH_4^+-N	Normal Season	0.025	0.025	0.032	0.002	6.9
	Flood season	0.025	0.025	0.025	0.000	0.0
	Dry season	0.131	0.025	0.495	0.130	99.3

3.1.2. Temporal Variation of Nitrogen Concentration in Influent Rivers

Table 2 summarizes the concentration changes of TN, NO_3^--N, and NH_4^+-N in the influent rivers of Baiyangdian Lake during different hydrological periods. Consistent with the temporal variation of nitrogen concentration in the lake water body, the average concentrations of TN, NO_3^--N, and NH_4^+-N show that the flood season (2.12 mg/L, 1.59 mg/L, and 0.074 mg/L, respectively) has lower concentrations compared to the dry season (3.17 mg/L, 2.38 mg/L, and 0.402 mg/L, respectively) and the normal water period (2.37 mg/L, 1.74 mg/L, and 0.553 mg/L, respectively). There are five, five, and six sampling sites in the influent rivers where TN concentration exceeds the Class III standard (1.0 mg/L) of the surface water environmental quality standard GB3838−2002 during the normal, flood, and dry seasons, respectively. This indicates that the pollution of TN in the influent rivers of Baiyangdian Lake is relatively severe. Overall, the coefficients of variation for TN, NO_3^--N, and NH_4^+-N in the influent rivers are lower during the normal water period (ice cover period) than during the flood and dry seasons. This suggests that the combined effects of non-point pollution caused by rainfall runoff and point-source pollution from human activities lead to differences in the sources of TN, NO_3^--N, and NH_4^+-N in different rivers, resulting in significant variations in their concentrations in the influent rivers during the flood and dry seasons.

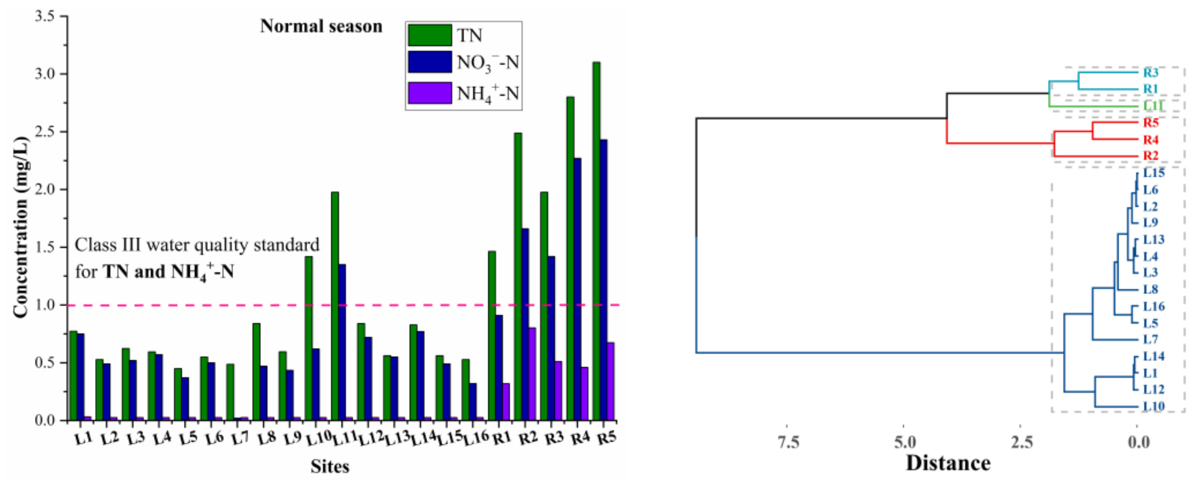
Table 2. Statistics of different nitrogen concentrations in inflow rivers of Baiyangdian Lake.

Parameters	Season	Mean (mg/L)	Min (mg/L)	Max (mg/L)	Standard Deviation	Coefficient of Variation (%)
TN	Normal season	2.37	1.46	3.10	0.654	27.6
	Flood season	2.12	0.557	4.06	1.26	59.6
	Dry season	3.17	0.907	5.25	1.53	48.4
NO_3^--N	Normal season	1.74	0.910	2.43	0.623	35.9
	Flood season	1.59	0.247	2.52	0.958	60.1
	Dry season	2.38	0.161	4.28	1.30	54.5
NH_4^+-N	Normal season	0.553	0.319	0.802	0.188	34.0
	Flood season	0.074	0.041	0.135	0.036	48.3
	Dry season	0.402	0.191	0.750	0.218	54.3

3.2. Spatial Variation Characteristics of Nitrogen Concentration in Baiyangdian Lake

(1) Spatial variation of nitrogen in Baiyangdian Lake during the normal season

The spatial variation of nitrogen in the Baiyangdian watershed generally shows that the concentration of nitrogen in the influent rivers is higher than that at the lake sites (Figure 3). The concentration of nitrogen at the central sites of the lake is lower than that at the surrounding sites, and the concentration at the northern sites of the lake is greater than that at the southern sites (Figures 2 and 3). The spatial variation at the Baiyangdian Lake sites specifically exhibits three distinct spatial characteristics.



(**a**) (**b**)

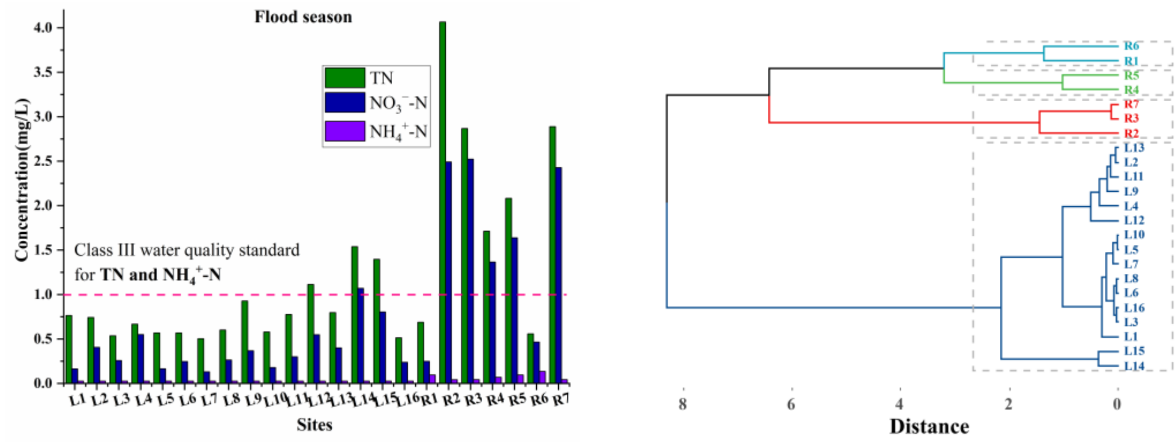
Figure 3. Spatial variation (**a**) and cluster analysis (**b**) of nitrogen in the Baiyangdian Lake during the normal season.

The first type is that the site is affected by a combination of aquaculture and domestic sewage, resulting in nitrogen concentrations higher than those at other sites. A representative site is L11, with TN and NO_3^--N concentrations of 1.98 mg/L and 1.35 mg/L, respectively. The second spatial variation characteristic is that the site is close to the influent rivers and villages, and it is significantly affected by the sewage from these sources, leading to higher water body concentrations compared to other internal lake sites. Representative sites include L1, L12, L10, and L14. The third spatial variation characteristic is for sites within the lake that are farther from villages and thus less affected by human activities, resulting in relatively lower nitrogen concentrations. Regarding the influent rivers, the sites are clustered into two categories. Sites R2, R4, and R5 have higher concentrations of TN (2.79 mg/L), NO_3^--N (2.12 mg/L), and NH_4^+-N (0.645 mg/L) compared to sites R1 and R3. This may be due to the presence of ecological wetlands on the west side of sites R1 and R3, where aquatic plants are abundant and can absorb and assimilate nitrogen from the water body.

(2) Spatial variation of nitrogen in Baiyangdian Lake during the flood season

As shown in Figure 4, during the flood season, the nitrogen in Baiyangdian Lake is significantly affected by rainfall, leading to a decrease in nitrogen concentrations at most lake and influent river sites. For the lake area, there are three main spatial variation patterns.

The first pattern involves sites L14 and L15, which are affected by a combination of non-point and point sources from the Xiaoyi River, resulting in higher nitrogen concentrations compared to other sites. The second pattern is observed at sites L9 to L13, which are located around aquaculture areas and thus have relatively higher nitrogen concentrations due to the impact of aquaculture activities. The third pattern is characterized by sites in the central part of the lake, which are less affected by human activities and therefore have relatively lower nitrogen concentrations.



(**a**) (**b**)

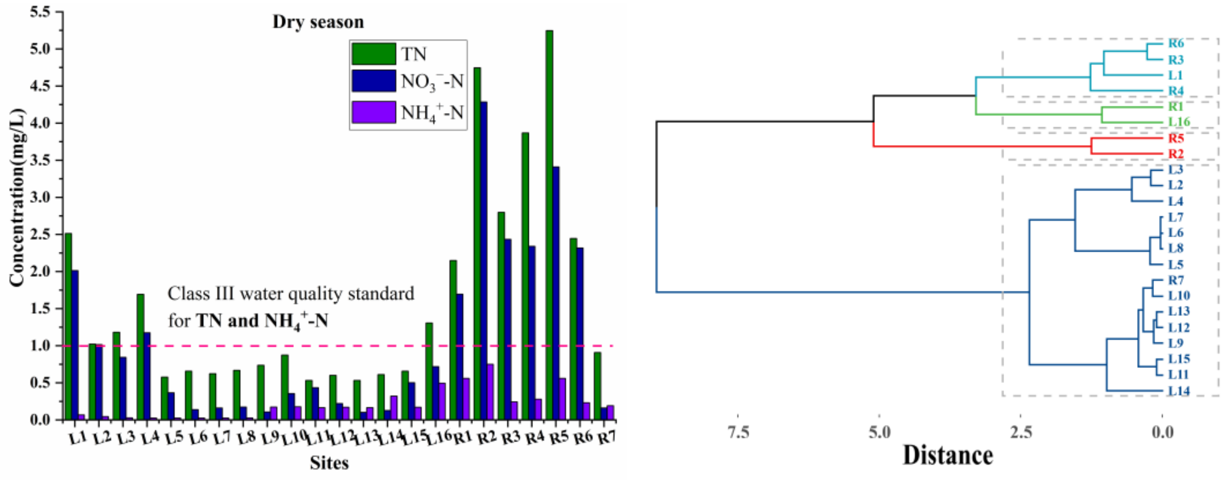
Figure 4. Spatial variation (**a**) and cluster analysis (**b**) of nitrogen in the Baiyangdian Lake during the flood period.

Regarding the influent rivers, they are spatially clustered into three categories. Overall, the average TN concentration at the first category of sites (3.27 mg/L) is higher than that at the second category (1.89 mg/L) and the third category (0.622 mg/L). The first category includes sites R2 (Cao River), R3 (Bao River), and R7 (Tang River), which are significantly affected by rainfall runoff and thus have higher nitrogen concentrations compared to other river sites. The second category includes sites R5 (Baigouyin River) and R4 (Xiaoyi River), where nitrogen concentrations decrease during the flood season due to the dilution effect of rainfall. The third category consists of sites R1 (Fu River) and R6 (Yellow River Diversion inlet). Site R1 has lower nitrogen concentrations due to the combined effects of upstream ecological wetland purification and rainfall dilution. Site R6, connected to the Xiaobai River as part of the Yellow River Diversion Project inlet, has better water quality.

(3) Spatial variation of nitrogen in Baiyangdian Lake during the dry season

As shown in Figure 5, during the dry season, the sites within Baiyangdian Lake are also clustered into three categories: The first category includes sites that are close to the Cao River (R2) and Baigouyin River (R5), such as sites L1–L4 and L16. Sites L1 and L16, with high nitrogen concentrations (exceeding 2.0 mg/L), are clustered with the influent rivers. These two rivers have been contaminated during the dry season (with TN concentrations reaching up to 4.75 mg/L and 5.25 mg/L), significantly impacting the surrounding water bodies. The second category consists of sites located downstream of the first category, influenced by the lake's self-purification capacity, resulting in a decrease in nitrogen concentrations. Representative sites include L5–L8. The third category comprises sites in the southern part of the lake, L9–L15, where human activities such as tourism and aquaculture are minimal or absent during the dry season (ice cover period), leading to relatively lower nitrogen concentrations in the water body.

For the influent rivers of Baiyangdian Lake, they are spatially clustered into three categories as well: the first category includes river sites R2 and R5, which are heavily affected by point-source pollution, with TN concentrations reaching 4.75 mg/L and 5.25 mg/L, respectively, significantly higher than other sites. The second category includes sites R3, R4, and R6, which are relatively more affected by point-source pollution, with nitrogen concentrations lower than those of the first category. The third category consists of sites R1 and R7. Site R1 has relatively lower concentrations due to the purification effects of upstream ecological wetlands, while site R7, being in a frozen state, is less affected by human activities, resulting in lower nitrogen concentrations. These spatial variations during the dry season highlight the differential impacts of various sources of pollution and the lake's self-purification processes on the nitrogen concentrations across different parts of Baiyangdian Lake.



(**a**) (**b**)

Figure 5. Spatial variation (**a**) and cluster analysis (**b**) of nitrogen in the Baiyangdian Lake during the dry period.

In summary, the spatial variation of nitrogen concentration in Baiyangdian Lake is not only influenced by point sources (domestic sewage) but also by the combined effects of agricultural non-point-source pollution caused by rainfall runoff and the replenishment of external water sources. For the overall lake area, the first type of spatial variation is that the nitrogen concentration in the northern part of the lake, which is close to the Baigouyin River replenishment and the agricultural non-point sources of the north, is higher than in the southern part of the lake, except for aquaculture areas. The second type of spatial variation is a gradual decrease in nitrogen concentration from the west to the east side of the lake, reaching the lowest at the outlet (site L7). As for the influent rivers, due to the different environments through which the rivers flow and the differences in upstream water sources, there is no clear regularity in their spatial characteristics.

3.3. Water Quality Assessment of Baiyangdian Lake

The single-factor pollution index method is a simple and effective way to determine the pollution status of water quality for a specific use, which can identify the category of water quality and the main pollution indicators. In this study, TN, NO_3^--N, and NH_4^+-N were selected, and the content limits specified in the Class III water quality standards of the surface water environmental quality standards were used as the evaluation criteria. The pollution indices of water quality factors at Baiyangdian Lake sites and influent rivers during the three hydrological periods were analyzed. The results (Table 3) indicate that, overall, the pollution indices of NO_3^--N and NH_4^+-N in Baiyangdian Lake and influent rivers are both < 1, suggesting that neither has shown pollution characteristics or reached a level that poses a threat to human health. However, the exceedance rates of TN in Baiyangdian Lake during the normal, flood, and dry seasons are 12.5%, 18.8%, and 31.3%, respectively, indicating a state of nitrogen pollution in Baiyangdian Lake. Moreover, the average pollution index of TN in the influent rivers during the three hydrological periods is greater than 2.0, indicating that the pollution of TN in the influent rivers is relatively severe and has a significant impact on the nitrogen pollution of Baiyangdian Lake.

Table 3. Pollution index values of different nitrogen forms in Baiyangdian Lake and its influent rivers.

Sites	Season	Parameters	Standard (mg/L)	Min (mg/L)	Max (mg/L)	Mean (mg/L)	Exceedance Rate (%)
Baiyangdian Lake	Normal season	TN	1.0	0.450	1.98	0.759	12.5
		NO_3^--N	10	0.002	0.135	0.056	0.0
		NH_4^+-N	1.0	0.025	0.032	0.025	0.0
	Flood season	TN	1.0	0.502	1.54	0.786	18.8
		NO_3^--N	10	0.013	0.107	0.038	0.0
		NH_4^+-N	1.0	0.025	0.025	0.025	0.0
	Dry season	TN	1.0	0.532	2.51	0.924	31.3
		NO_3^--N	10	0.010	0.201	0.053	0.0
		NH_4^+-N	1.0	0.025	0.495	0.131	0.0
River	Normal season	TN	1.0	1.46	3.10	2.37	100.0
		NO_3^--N	10	0.090	0.240	0.174	0.0
		NH_4^+-N	1.0	0.320	0.800	0.553	0.0
	Flood season	TN	1.0	0.560	4.06	2.12	71.4
		NO_3^--N	10	0.020	0.250	0.159	0.0
		NH_4^+-N	1.0	0.040	0.130	0.074	0.0
	Dry season	TN	1.0	0.910	5.25	3.17	85.7
		NO_3^--N	10	0.020	0.430	0.238	0.0
		NH_4^+-N	1.0	0.190	0.750	0.402	0.0

4. Discussion

4.1. Comparison of Nitrogen Concentrations in Different Types of Lakes

Baiyangdian Lake, the largest shallow lake in the North China Plain, is known as the "Pearl of North China". The quality of its water directly affects the ecological safety of the Xiong'an New Area and also impacts the regional ecological balance and biodiversity of the Beijing–Tianjin–Hebei urban agglomeration [19]. In recent years, national and local governments have carried out comprehensive management of Baiyangdian Lake and its tributaries, and ecological water replenishment measures, such as the Yellow River Diversion Project, have been implemented, leading to continuous improvement in the water quality of Baiyangdian Lake. In this study, we compared the nitrogen levels in Baiyangdian Lake with those in other lakes, including Tai Lake [20], Chao Lake [21], Dian Lake [22], Lugu Lake [23], and Bosten Lake [24] (Figure 6).

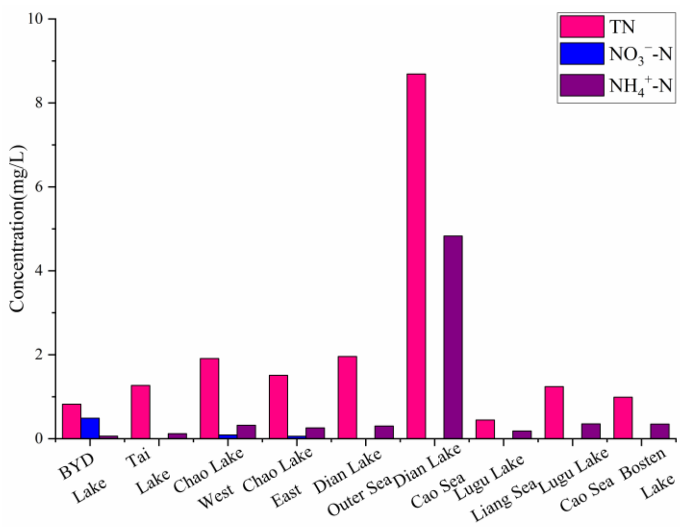


Figure 6. Comparison of nitrogen concentrations in lakes from different regions of China.

Baiyangdian Lake is located in the Xiong'an New Area, which has developed rapidly in recent years, and the national governance efforts have been significant, with a population density of about 700 people per square kilometer in the basin. The Tai Lake and Chao Lake basins are in more developed areas with larger population densities, at 650 and 420 people per square kilometer, respectively. Dian Lake and Lugu Lake are both plateau lakes located in the southwestern region of China. Dian Lake is situated to the southwest of Kunming with a population density of 320 people per square kilometer, while Lugu Lake, located at the junction of Sichuan and Yunnan, has a lower population density of 42 people per square kilometer. Bosten Lake is in the northwest region of China, where social and economic development are relatively lagging, with a population density of about 3 people per square kilometer. Compared to Tai Lake and Chao Lake, which have similar population densities, Baiyangdian Lake has lower concentrations of TN and ammonium nitrogen. Compared to the plateau lakes, Baiyangdian Lake has lower TN and ammonium nitrogen concentrations than Dian Lake but higher TN than Lugu Lake, which has a smaller population density. When compared to Bosten Lake, which has a lower population density, the concentration of TN in the Baiyangdian Lake is slightly lower. This differs somewhat from previous research findings. Previous studies have found that nitrogen concentrations in aquatic environments are positively correlated with the population density within the basin [25,26]. In recent years, comprehensive water quality management by national and local governments has led to year-by-year improvements in the water quality of Baiyangdian Lake. Additionally, compared to these other lakes, Baiyangdian Lake is abundant in reeds and other aquatic plants, and the slow water flow in Baiyangdian Lake facilitates the absorption of nitrogen elements by these plants. It is noteworthy that the concentration of ammonium nitrogen in Baiyangdian Lake is lower than that in these other lakes, which may be related to plants' preference for utilizing the more easily absorbed and assimilated NH_4^+-N [27]. Furthermore, previous research has found that the dissolved oxygen (DO) concentration in Baiyangdian Lake is relatively high, indicating that strong nitrification may occur in the water body [28].

4.2. Identification of Nitrogen Sources in Baiyangdian Lake

Nitrogen pollution sources in the aquatic environment can be divided into point sources and non-point sources. Point source pollution typically includes industrial wastewater, urban domestic sewage, leachate from municipal solid waste, leakage from septic tanks and sewage pipelines in suburban areas, and seepage from animal farms; non-point-source pollution generally includes surface runoff pollution, irrigation with wastewater, and the application of chemical fertilizers and manure. Researchers commonly categorize nitrogen pollution sources into five types: agricultural fertilizers, animal manure, industrial wastewater and domestic sewage, soil nitrogen, and atmospheric deposition [29].

4.2.1. Ion Ratio Method for Source Tracing

Cl^- serves as an important auxiliary tool for identifying the sources of nitrogen in an aquatic environment. Its inert nature makes it less susceptible to the physical, chemical, and biological processes in the water body, making it a good indicator of sewage input [30]. Many scholars have used the relationship between $[NO_3^-]/[Cl^-]$ and $[Cl^-]$ to identify the sources of NO_3^- in an aquatic environment. Yao et al. (2007) showed that high concentrations of $[Cl^-]$ and low $[NO_3^-]/[Cl^-]$ ratios indicate that NO_3^- primarily comes from domestic sewage and feces [31]; low concentrations of $[Cl^-]$ and high $[NO_3^-]/[Cl^-]$ ratios suggest that NO_3^- mainly originates from fertilizers; low values of both $[NO_3^-]/[Cl^-]$ and $[Cl^-]$ indicate that NO_3^- primarily comes from soil organic nitrogen. To determine the sources of nitrogen in Baiyangdian Lake, this study plotted the relationship between $[NO_3^-]/[Cl^-]$ and $[Cl^-]$ (Figure 7). The $[NO_3^-]/[Cl^-]$ values in Baiyangdian Lake range from 0 to 0.080, with average values of 0.013, 0.017, and 0.019 for the normal, flood, and dry seasons, respectively. The low ratios suggest that fertilizers are not the main source of NO_3^- in Baiyangdian Lake. Overall, the low $[NO_3^-]/[Cl^-]$ and high $[Cl^-]$ values in

Baiyangdian Lake indicate that NO_3^- in the water body is mainly influenced by animal manure and domestic sewage. Previous studies have found that unpolluted water bodies generally have Cl^- concentrations below 49.7 mg/L [12]. In Baiyangdian Lake, 77% of the sampling points have Cl^- concentrations above 49.7 mg/L (the average Cl^- concentrations measured during the three sampling periods for the normal, flood, and dry seasons are 117 mg/L, 72.8 mg/L, and 86.0 mg/L, respectively), further indicating that manure and domestic sewage are potential sources of NO_3^- in Baiyangdian Lake. Seasonally, the $[NO_3^-]/[Cl^-]$ ratio is highest in the dry season, followed by the flood season, and then the normal season. The $[Cl^-]$ values vary significantly across different sampling periods, with the highest concentration in the normal season and the lowest in the flood season, suggesting more severe pollution from domestic sewage and feces during the normal season. Notably, during the flood season, the $[NO_3^-]/[Cl^-]$ values at sites L14 and L15 in the southeast area are relatively high, with Cl^- concentrations below 1.40 mmol/L, possibly due to the predominance of agricultural land use and fewer man-made structures on the southeast shore of Baiyangdian Lake. The abundant rainfall in July may lead to stronger leaching of soil, and surface runoff carries nitrogen from the fields into the lake area. In the dry season, the $[NO_3^-]/[Cl^-]$ values at sites L1, L2, and L4 in the north are relatively high, with Cl^- concentrations ranging from 1.73 to 1.84 mmol/L, possibly due to the concentrated distribution of farmland in the northern area, where agricultural activities have an important impact on the water quality at these sites.

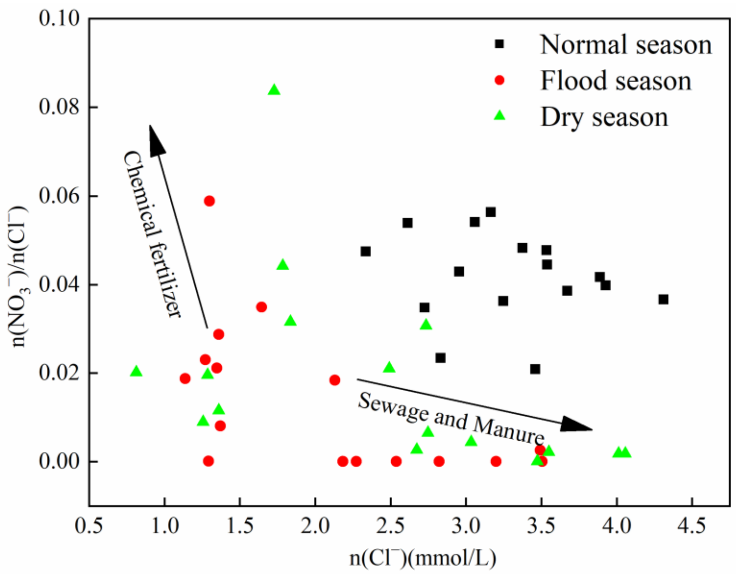


Figure 7. $[Cl^-]$ and $[NO_3^-]/[Cl^-]$ relationship for Baiyangdian Lake.

4.2.2. Identification of Nitrogen Pollution Sources in Baiyangdian Lake Using PCA

This study utilized PCA to identify the pollution sources in Baiyangdian Lake across three hydrological periods. During the normal water period, the first principal component (PC1) accounted for 37.4% of the total variance (Figure 8), and the variables that showed strong positive correlations with PC1 included TN, NO_3^--N, Ca^{2+} and SO_4^{2-}. It is generally believed that TN and NO_3^--N in the aquatic environment primarily originate from human activities, such as the application of agricultural fertilizers, animal manure, soil nitrogen, sewage, and atmospheric deposition [32], while SO_4^{2-} mainly comes from fertilizers, sewage, evaporite dissolution, rainfall, and industrial emissions [33]. Given the high concentration of TN in Baiyangdian Lake and the relative independence of PC1 and PC2, PC1 represents the influence of manure and fertilizer on the water quality of Baiyangdian Lake. Variables that showed strong positive correlations with the second principal component (PC2) were Cl^- and Na^+, and a strong negative correlation was observed with NH_4^+-N. Typically, NH_4^+-N mainly comes from domestic sewage and fertilizers, and

Cl^- primarily originates from domestic sewage, fertilizers, manure, road deicing salt, and the dissolution of natural minerals [34]. In this study, there were no rock salts, and no road deicing salts were used in that season. The high concentration of Cl^- in Baiyangdian Lake is consistent with the characteristics of domestic sewage. Additionally, domestic sewage contains a certain amount of Na^+ [35]. This further indicates that the water body of Baiyangdian Lake is affected by domestic sewage, and therefore, PC2 indicates that the water quality of Baiyangdian Lake was impacted by domestic sewage.

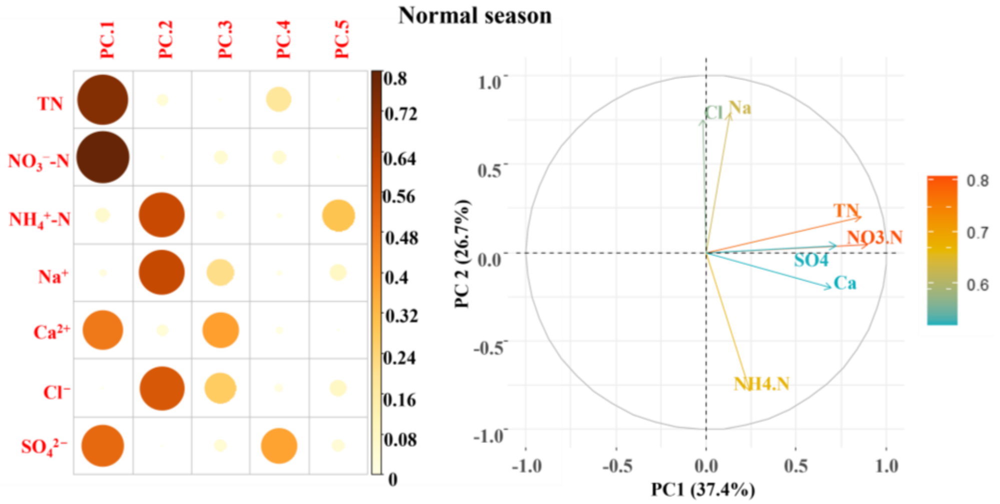


Figure 8. Principal component analysis results for Baiyangdian Lake during the normal period.

During the flood season, the first principal component (PC1) accounted for 65.5% of the total variance (Figure 9), with strong positive correlations observed with Na^+, SO_4^{2-}, and Cl^-, and strong negative correlations with TN, NO_3^--N, and Ca^{2+}. As previously mentioned, Na^+ and Cl^- in Baiyangdian Lake primarily originate from domestic sewage, while TN and NO_3^--N mainly come from manure and fertilizers. Therefore, PC1 represents the influence of domestic sewage, manure, and fertilizer on the Baiyangdian Lake. The second principal component (PC2) showed a strong positive correlation with NH_4^+-N. However, during the flood season, the concentration of NH_4^+-N in Baiyangdian Lake is relatively low, close to the detection limit, indicating significant nitrification occurring in the water body. Thus, PC2 represents the impact of nitrification on the nitrogen in Baiyangdian Lake.

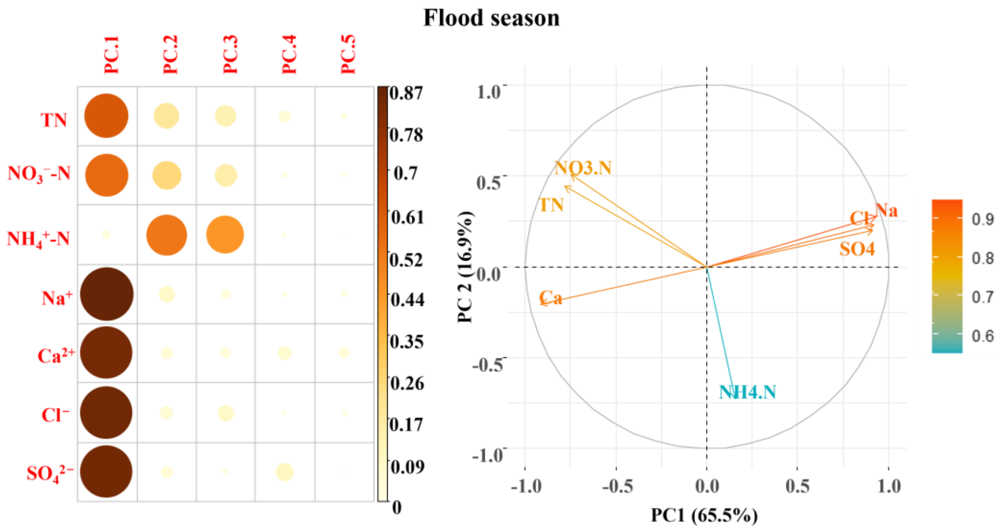


Figure 9. Principal component analysis results for Baiyangdian Lake during the flood period.

During the dry season (ice cover period), the first principal component (PC1) accounted for 39.5% of the total variance (Figure 10). There was a strong positive correlation with Na^+, a strong negative correlation with TN and NO_3^--N, and a moderate positive correlation with NH_4^+-N and Cl^-. This suggests that the Baiyangdian Lake was influenced by domestic sewage. Furthermore, the negative correlation between NH_4^+-N and both TN and NO_3^--N indicates that nitrification and denitrification processes were occurring in the water body. The second principal component (PC2) showed a strong positive correlation with SO_4^{2-} and Cl^-, and a moderate positive correlation with Ca^{2+}, TN, and NO_3^--N, indicating that PC2 represents the influence of manure and fertilizer on the Baiyangdian Lake.

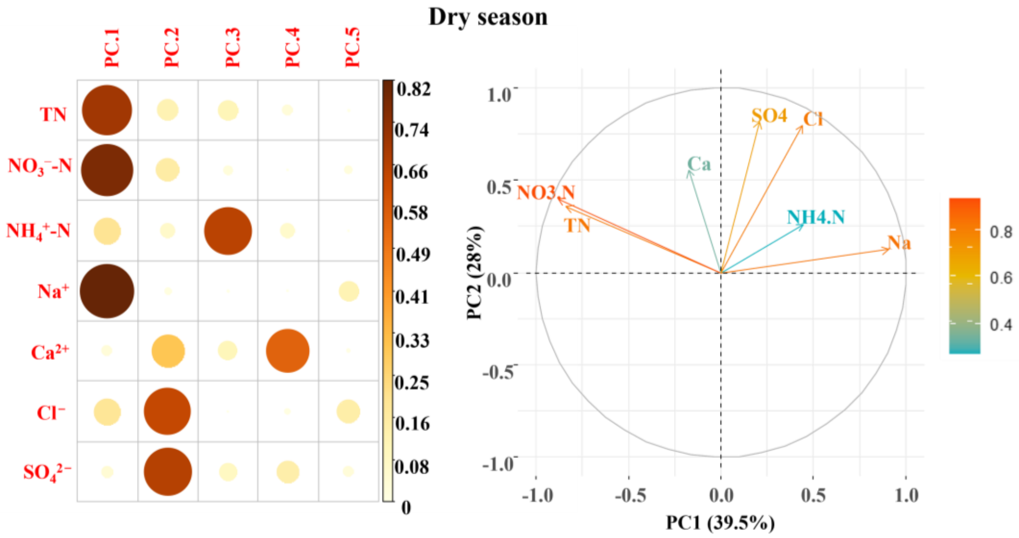


Figure 10. Principal component analysis results for Baiyangdian Lake during the dry period.

Overall, the main sources of nitrogen pollution in the Baiyangdian water body during the three hydrological periods are domestic sewage, manure, and fertilizers. However, the contribution of pollution sources to the nitrogen in the water body varies to some extent during different hydrological periods. During the dry season, due to the absence of rainfall runoff to drive the process, it is difficult for residual fertilizers in the fields to enter the water body, hence the main source of pollution during this period is domestic sewage. In contrast, during the flood and normal water periods, rainfall runoff and leaching carry manure and fertilizers from the fields into Baiyangdian Lake, making them the primary sources of nitrogen in the water body during these periods. Therefore, the main measures to control the increase of nitrogen concentration in Baiyangdian Lake are to prevent direct discharge of domestic sewage, implement scientific fertilization methods, and prevent agricultural non-point-source pollution.

5. Conclusions

The study provides a comprehensive assessment of nitrogen pollution in Baiyangdian Lake, identifying significant seasonal and spatial variations in nitrogen concentrations. The dry season exhibited the highest average total nitrogen (TN) levels, with 31.3% of sites surpassing national water quality standards, underscoring the lake's vulnerability to nitrogen pollution. Spatial analysis revealed that northern areas and sites proximal to influent rivers are more significantly impacted, likely due to point-source pollution and agricultural non-point-source pollution exacerbated by rainfall runoff. Utilizing the ion ratio method and principal component analysis (PCA), domestic sewage and manure were pinpointed as the predominant sources of nitrogen pollution, with agricultural activities also contributing to nitrogen levels. The study suggests that the water quality of the Baiyangdian Lake is relatively good compared to other lakes with similar human activity intensities, indicating effective management measures. To sustain the water quality and ecological balance, it is recommended to enhance monitoring and implement nitrogen reduction strategies. This includes curbing direct sewage discharge, adopting scientific fertilization strategies that are tailored to the specific conditions of time, location, and crop types, and bolstering ecological restoration efforts such as wetland recovery and vegetation restoration. Our research provides a scientific foundation for ongoing management of and pollution prevention in Baiyangdian Lake.

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